[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, REED COLLEGE]

Comparative Activation of Nucleophilic Substitution in 4-Substituted-2-nitrochlorobenzenes[1]

BY J. F. BUNNETT,[1a] FRANKLIN DRAPER, JR., P. R. RYASON, PAUL NOBLE, JR., R. G. TONKYN AND R. E. ZAHLER

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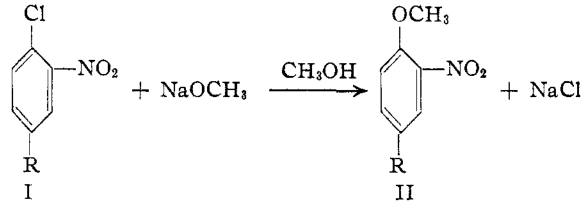
For reactions of three 4-substituted-2-nitrochlorobenzenes with sodium methoxide, rate coefficients have been determined at 25, 35 and 45°. These show that a number of activating groups stand in the following order of activating power: $NO_2 > CH_3SO_2 > (CH_3)_3N^+ > CH_3CO > Cl > H$. This is the first evidence of activation of aromatic nucleophilic substitution by the trimethylammonio group.

For some time it has been known that certain substituent groups activate aromatic nucleophilic substitution reactions.[2] However, there has been little information on which to base quantitative comparisons of the activating effects of groups, although recently some data regarding activating groups has been published by Bunnett and Levitt[3a] and regarding deactivating groups by Berliner and Monack.[3b]

In the present work, rate coefficients have been determined for the reactions of three 4-substituted-2-nitrochlorobenzenes with methanolic sodium methoxide at 25, 35 and 45°.



The rate coefficients for 25°, together with energy and entropy of activation values, are displayed in Table I. The table includes, for comparison, certain data from the literature.

TABLE I

REACTIONS OF 4-SUBSTITUTED-2-NITROCHLOROBENZENES WITH SODIUM METHOXIDE

Group in 4-position	Rate coefficient at 25° l. mole^{-1} sec.$^{-1}$ × 10^4	On scale k_{NO_2} = 1000	ΔE, kcal.	$\Delta S‡$, cal./deg.
NO_2[a]	250	1000	16.8 ± 0.2	−11.3 ± 0.7
CH_3SO_2	26.5	106	18.6 ± .3	− 9.7 ± 1.0
$(CH_3)_3N^+$	8.23	33	20.3 ± .2	− 6.3 ± 0.7
CH_3CO	3.11	12.4	19.1 ± .4	−12.3 ± 1.3
Cl[a]	0.0175	0.07	22.8	−10.1
H[a]	0.0015	0.006	[b]	[b]

[a] Values from the literature; for sources, see ref. 2, pp. 353 and 357. [b] k_{25} is calculated from literature values for higher temperatures. The values do not appear to be sure enough to justify calculation of energy and entropy of activation.

Our earlier contribution[3a] reported rate coefficients for the reactions of some *p*-substituted bromobenzenes with piperidine in benzene at 99°; the values found are shown in Table II. Together, these tables establish the following order of activating power for the groups involved: $NO_2 > CH_3SO_2 > (CH_3)_3N^+ > CN > CH_3CO > Cl > H$.

TABLE II

REACTIONS[3a] WITH PIPERIDINE IN BENZENE AT 99°

Compound	Rate coefficient l. mole^{-1} sec.$^{-1}$ × 10^7	On scale k_{NO_2} = 1000
p-Bromonitrobenzene	64.5	1000
p-Bromophenyl methyl sulfone	3.40	52.7
p-Bromobenzonitrile	1.98	30.7
p-Bromoacetophenone	0.86	13.3

Table I contains, to our knowledge, the first evidence of activation of aromatic nucleophilic substitution by an ammonio[4] or substituted ammonio group.[5,6] The magnitude of its activating effect is of particular interest because the trimethylammonio group cannot exert any electronic effect except an inductive effect. Activation of nucleophilic substitution in aromatic compounds by substituted ammonio groups has been expected because of their strong deactivation of electrophilic substitution.[8] But whereas trimethylammonio deactivates nitration more strongly than does nitro,[9]

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[1] Presented at the American Chemical Society Meeting, Boston, Mass., April, 1951.

[1a] Chemistry Department, University of North Carolina, Chapel Hill, N. C.

[2] Information regarding the activating effects of various groups has been summarized by J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 307 (1951).

[3] (a) J. F. Bunnett and A. Levitt, THIS JOURNAL, **70**, 2778 (1948); (b) E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952).

[4] Chemists have at times called the $-NH_3^+$ substituent group the "ammonium" or "ammonium salt" group. These names have not gained wide acceptance and use of them has often been avoided by use of the formula of the group or in some other way. We have proposed (ref. 2, p. 291) for the $-NH_3^+$ group the designation "ammonio" which signifies both its chemical nature and its substituent character, and yet offers no possibility for confusion with the names of ions or molecules. Analogously, the $(CH_3)_2S^+-$ substituent group would be called the "dimethylsulfonio" group.

[5] The action of concentrated hydrochloric acid on 2,4,6-tribromoaniline to produce 2,4,6-trichloroaniline (R. Wegscheider, *Monatsh.*, **18**, 329 (1897)) is probably a nucleophilic displacement of bromine by chloride, activated in part by the ammonio group in the amine hydrochlorides. However, Wegscheider's experiments cannot be accepted as proof of such an activating effect. W. S. Emerson, F. B. Dorf and A. J. Deutschman, THIS JOURNAL, **62**, 2159 (1940), believed the reductive removal of bromine from 2,4,6-tribromoaniline in acid solution to be a case of activation by the ammonio group. It has since been shown by R. B. Sandin and J. R. L. Williams, *ibid.*, **69**, 2747 (1947), that this reaction is an electrophilic displacement of halogen with activation by the amino group of the free amine.

[6] In an early attempt in this Laboratory to demonstrate activation by the trimethylammonio group, Mr. Horst Weber found that the action of boiling ethanolic sodium ethoxide on *p*-bromophenyltrimethylammonium iodide produced not the expected ethoxy compound, but rather *p*-bromodimethylaniline; *cf.* ref. 7.

[7] D. Vorlander and E. Spreckels, *Ber.*, **52**, 309 (1919).

[8] *Cf.* G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 262.

[9] (a) T. G. Bonner, M. E. James, A. M. Lowen and G. Williams, *Nature*, **163**, 955 (1949); (b) J. C. D. Brand and R. P. Paton, *J. Chem. Soc.*, 281 (1952).

it activates replacement of *p*-chlorine by methoxide less strongly.

This apparent anomaly is probably a consequence of the different polarization and polarizability effects of the trimethylammonio and nitro groups. *Deactivation* is principally caused by polarization effects[10] and the trimethylammonio group evidently polarizes the ring somewhat more strongly than the nitro group. *Activation* results not only from the polarization effects of groups, but also from their polarizability effects, that is, from the capacity of groups to accommodate the positive or negative charge of the transition state.[10] In the present case the nitro group has a large polarizability effect (a large capacity to accommodate a negative charge) while the trimethylammonio group has a small polarizability effect, owing largely to its inability to form a double bond with the ring carbon. The considerable advantage gained by the nitro group in regard to its polarizability effect enables it to overcome the slight disadvantage in regard to its polarization effect so that it becomes, over-all, much more powerful than the trimethylammonio group in activating nucleophilic substitution.

Figure 1 is a plot of log k_{25} against sigma[11] for the various groups. All but one of the points lie close to the line which has been drawn. The slope of this line, or ρ for this reaction, is +3.9, a very high value[15] though not so high as that (+4.95) for the reactions of 4-substituted-2-nitrobromobenzenes with piperidine.[3b] The explanation for the divergence from the line of the point for the trimethylammonio group is to be found in Table I in the high entropy of activation for the reaction of I, R = $(CH_3)_3N^+$. Possibly the fact that this is a reaction between a cation and an anion, whereas the others are reaction of anions with neutral molecules, accounts for its high entropy of activation.[16b]

Syntheses and Product Identification.—3-Nitro-4-chlorophenyl methyl sulfone and 3-nitro-4-chloroacetophenone were made by usual methods. Two routes to 3-nitro-4-chlorophenyltrimethylammonium iodide were used. Initially, the reaction of 3-nitro-4-chlorodimethylaniline with methyl iodide was employed, but the synthesis was laborious. Larger amounts were made by nitrating *p*-chlorophenyltrimethylammonium picrate in concentrated sulfuric acid and converting the resulting picrate to the desired iodide. To our knowledge, this is one of the few cases in which nitration of an aromatic quaternary ammonium salt has been used for preparative purposes.

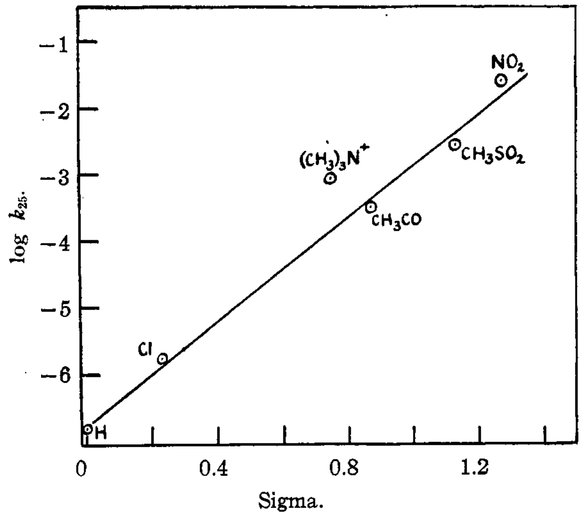

Fig. 1.—A plot of log k_{25} *vs.* σ.

Each of the three compounds studied kinetically was allowed to react with methanolic sodium methoxide at room temperature, and from each reaction the corresponding anisole derivative was isolated. That dealkylation of 3-nitro-4-chlorophenyltrimethylammonium iodide did not occur in reaction with methoxide[6,7] was further established by the fact that, at 45°, the consumption of methoxide ion was equal to the release of chloride ion.

Experimental[17]

3-Nitro-4-chloroacetophenone, m.p. 98–99° (lit.[18] 99–100°), was prepared by nitration of *p*-chloroacetophenone.

3-Nitro-4-chlorophenyl Methyl Sulfone.—*p*-Chlorophenyl methyl sulfone, m.p. 95–97° (lit.[19] 96°) was obtained from *p*-chlorobenzenesulfonyl chloride by the method of Oxley, Partridge, Robson and Short.[20] It was nitrated by the method of Twist and Smiles,[21] furnishing 3-nitro-4-chlorophenyl methyl sulfone, m.p. 119–120° after recrystallization from a mixture of equal volumes of ethanol and carbon tetrachloride, as fine white crystals.

Anal. Calcd. for $C_7H_6ClNO_4S$: C, 35.68; H, 2.57. Found: C, 35.58; H, 2.70.

The isomeric 2-nitro-4-chlorophenyl methyl sulfone is known[22]; it melts at 143°.

Preparation of 3-Nitro-4-chlorophenyltrimethylammonium Iodide. A. Involving Nitration of the Tertiary Amine.—**p-Chloro-N,N-dimethylaniline** was prepared in 75% yield by van Duin's[23] procedure for *o*-chloro-N,N-dimethylaniline and was converted to **3-nitro-4-chloro-N,N-dimethylaniline** in 89% yield by Pinnow's[24] nitration procedure. Methylation: in a Coca Cola bottle there were placed 4.0 g. of 3-nitro-4-chloro-N,N-dimethylaniline, 15 ml. of methyl iodide and 50 ml. of methanol, and the neck was sealed by a rubber stopper tightly wired in place. After 24 hours at 57–72°, the bottle was cooled, opened and the crystalline yellow product collected by filtration and washed with ether; weight: about 5 g., m.p. 163–166°. After two recrystallizations from water there remained 4.29 g. (63%), m.p. 165–

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(10) Reference 2, p. 320.

(11) σ-Values derived from acidity constants of anilinium ions have been used as follows: for NO_2, +1.27 and for Cl, +0.23 (ref. 12); for CH_3SO_2, +1.13 (ref. 13); for $(CH_3)_3N^+$, +0.75 (ref. 14); for CH_3CO, +0.87 (ref. 12 and 13). Equilibrium between anilinium ions and aniline molecules is, like the rate of nucleophilic substitution, particularly sensitive to the conjugative power of groups in the para position.

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(13) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

(14) J. D. Roberts, R. A. Clement and J. J. Drysdale, *ibid.*, **73**, 2181 (1951).

(15) This value must be regarded as approximate because of uncertainties in the σ-values used.

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, (a) p. 199; (b) p. 435.

(17) Melting points are uncorrected. Carbon and hydrogen analyses by Dr. Carl Tiedcke.

(18) N. J. Leonard and S. N. Boyd, *J. Org. Chem.*, **11**, 415 (1946).

(19) C. J. Miller and S. Smiles, *J. Chem. Soc.*, **127**, 231 (1925).

(20) P. Oxley, M. W. Partridge, T. D. Robson and W. F. Short, *ibid.*, 767 (1946).

(21) R. F. Twist and S. Smiles, *ibid.*, **127**, 1249 (1925).

(22) T. Zincke and J. Baeumer, *Ann.*, **416**, 86 (1918).

(23) C. F. van Duin, *Rec. trav. chim.*, **51**, 878 (1932); *C. A.*, **26**, 5550 (1932).

(24) J. Pinnow, *Ber.*, **31**, 2982 (1898).

166° (dec.). The sample for iodide analysis was prepared by method B.

Anal. Calcd. for $C_9H_{12}O_2N_2ClI$: C, 31.55; H, 3.54; I, 37.04. Found: C, 31.96; H, 3.63; I, 37.1.

An English paper[25] reports m.p. 176° for this compound; in our laboratories no samples have melted above 165–166° (uncor.) when the m.p. is determined in a capillary tube in the usual way. Samples prepared by methods A and B showed no depression of mixed melting point.

B. Involving Nitration of the Quaternary Ammonium Salt. *p*-Chlorophenyltrimethylammonium Picrate.—To 26 g. of *p*-chloroaniline in 75 ml. of methanol, 90 g. of methyl sulfate was added in portions, the mixture being neutralized with 30% sodium hydroxide just before each addition.[23] The next day the solution was neutralized, filtered to remove solid impurities and treated with a solution of 58.6 g. of picric acid (containing 10% of water) in 250 ml. of warm methanol. A bright yellow precipitate separated; recrystallized from ethanol, it weighed 73.5 g. and had m.p. 183–196°. This crude picrate was used for nitration; small samples were further recrystallized and the m.p. rose to 199–199.5°.

3-Nitro-4-chlorophenyltrimethylammonium Picrate.—Forty-two and a half grams of *p*-chlorophenyltrimethylammonium picrate was dissolved in 430 ml. of concentrated sulfuric acid. To this solution, cooled to 0° and stirred constantly, 22 ml. of nitric acid (sp. gr. 1.42) was added dropwise during about 40 minutes. After addition was complete, the cooling-bath was removed and stirring continued an additional 2 hours and 40 minutes. The mixture was poured onto ice and made basic with concentrated ammonia solution; the resulting golden orange precipitate weighed 46.9 g., m.p. 171–175°.

3-Nitro-4-chlorophenyltrimethylammonium Iodide.—A suspension of 5 g. of 3-nitro-4-chlorophenyltrimethylammonium picrate in 40 ml. of 6 *M* hydrochloric acid was extracted with 50 ml. of benzene and then twice with 25-ml. portions of the same solvent (to remove picric acid). The aqueous layer was concentrated by vacuum evaporation to a thin sirup to which a saturated solution of potassium iodide was added in excess; a yellow, flocculent precipitate formed. Recrystallization of it from 50% methanol was made more efficient by addition of saturated potassium iodide solution to the cooled filtrate; yield 2.1 g., m.p. 164–164.5° (dec.). The over-all yield from *p*-chloroaniline was 49%.

Isolation Experiments. 3-Nitro-4-methoxyphenyltrimethylammonium Iodide.—The solution remaining, after withdrawal of samples for titration, from one kinetic run on 3-nitro-4-chlorophenyltrimethylammonium iodide was allowed to stand several days at room temperature and then was evaporated almost to dryness in a vacuum with mild external heating. Yellow-orange crystals formed; after recrystallization from water they melted at 174° with decomposition.

TABLE III

TYPICAL RUN: REACTION OF 3-NITRO-4-CHLOROACETOPHENONE WITH SODIUM METHOXIDE AT 45.0°

Initial concentration of ketone, 0.0150 molar; initial concentration of methoxide, 0.0150 molar; volume of each sample, 50.567 ml. Each sample was quenched in 10.086 ml. of 0.1078 molar hydrochloric acid (1.087×10^{-3} mole). 0.1041 molar sodium hydroxide was used for titration.

Time, sec. × 10^{-4}	NaOH required Ml.	NaOH required Mole × 10^3	(Mole HCl less moles NaOH) × 10^3	$1/(a - x)$ or 50.567/(moles $NaOCH_3$ unused × 10^3)
0.000	3.42	0.3560	0.7313	69.15
.360	4.17	.4341	.6532	77.41
.720	4.81	.5007	.5866	86.20
1.080	5.33	.5549	.5324	94.98
1.440	5.71	.5944	.4929	102.59
1.800	6.10	.6350	.4523	111.80
2.160	6.37	.6631	.4242	119.21

The method of least squares yields a value for *k* of 23.3 l. mole^{-1} sec.$^{-1}$.

Anal. Calcd. for $C_{10}H_{15}IN_2O_3$: C, 35.52; H, 4.47. Found: C, 35.43, 35.61; H, 4.60, 4.66.

3-Nitro-4-methoxyacetophenone.—The solutions remaining, after withdrawal of samples for titration, from a number of reactions of methoxide with 3-nitro-4-chloroacetophenone were combined and evaporated to a small volume. A white solid separated; recrystallized from ethanol, it melted at 97–99°. This is in agreement with the m.p. 99.5° reported[26] for 3-nitro-4-methoxyacetophenone, but is also virtually the same as that of the starting material. However, the mixed m.p. with 3-nitro-4-chloroacetophenone was strongly depressed and the compound gave a negative test for chlorine.

3-Nitro-4-methoxyphenyl Methyl Sulfone.—From the residues from the kinetic study, a white crystalline solid of m.p. 144.5–145.5° (after recrystallization from ethanol) was isolated.

TABLE IV

RATE COEFFICIENTS FOUND FOR REACTIONS WITH SODIUM METHOXIDE

Compound	Temp., °C.	Rate coefficient, l. mole^{-1} sec.$^{-1}$ × 10^4 From individual runs	Mean	Average deviation, %
3-Nitro-4-chloroacetophenone	25.0	2.98		
		(4.66)[a]		
		3.09		
		3.11		
		3.20		
		3.17	3.11 ± 0.06	2.0
	35.0	9.05		
		9.23		
		9.19		
		8.96	9.11 ± .10	1.1
	45.0	23.3		
		22.8		
		24.8		
		23.7	23.7 ± .6	2.5
3-Nitro-4-chlorophenyltrimethylammonium iodide	25.0	8.06		
		(7.49)[a]		
		8.32		
		8.32	8.23 ± .12	1.4
	35.0	25.8		
		(24.8)[a]		
		25.6		
		25.7	25.7 ± .1	0.4
	45.0	71.5		
		71.8		
		70.6	71.3 ± .5	0.7
3-Nitro-4-chlorophenyl methyl sulfone	25.0	(30.1)[a]		
		27.2		
		25.8		
		25.8		
		26.8		
		26.8		
		26.4	26.5 ± .5	1.9
	35.0	75.8		
		76.2		
		76.5		
		76.4	76.2 ± .2	0.3
	45.0	192		
		197		
		186		
		194		
		192		
		(172)[a]	192 ± 3	1.6

[a] Discarded value, not used in calculating mean.

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[25] R. D. Haworth, A. H. Lamberton and D. Woodcock, *J. Chem. Soc.*, 187 (1947).

[26] F. Stockhausen and L. Gattermann, *Ber.*, **25**, 3521 (1892).

Anal. Calcd. for $C_8H_9NO_5S$: C, 41.55; H, 3.92. Found: C, 41.58, 41.52; H, 3.90, 4.09.

Reaction of 3-Nitro-4-chlorophenyltrimethylammonium Iodide with Sodium Methoxide at 45°.—The purpose was to detect the possible occurrence of demethylation[6,7] as a side reaction. A solution of 7.50×10^{-4} mole of the quaternary ammonium salt and 7.75×10^{-4} mole of sodium methoxide in 50 ml. of methanol was kept overnight at 45°. The reaction was quenched with a measured excess of sulfuric acid and back-titrated with standard sodium hydroxide using a *p*H meter. The curve had only one break, which was very sharp. 6.33×10^{-4} mole of methoxide had been consumed in the reaction. The solution was acidified and halide ion precipitated with silver nitrate; the weight of the precipitate showed that 6.29×10^{-4} mole of chloride ion had been formed. A separate potentiometric titration showed that the expected product of demethylation, 3-nitro-4-chlorodimethylaniline (obtained by synthesis), did not exhibit basic properties under the conditions of this titration.

Rate Measurements.—In each kinetic run the initial concentration of the aromatic compound and of sodium methoxide was 0.015 molar. The necessary amount of aromatic compound was weighed to the nearest tenth of a milligram and dissolved in magnesium-dried methanol in a volumetric flask. Just previous to each run, the required volume of standard sodium methoxide solution was added to the flask contents. In early runs the reaction mixture was made up to the mark with methanol at room temperature, and the temperature corrections for flask and pipet volumes were introduced into the rate calculations. Later reaction mixtures were made up to volume at the reaction temperature after temperature equilibration of both the reactants in methanol and the methanol diluent. After dilution, the flask was thoroughly shaken and placed in the thermostat (constant to ±0.05°).

The time of release of each pipetted sample (always one-tenth of the original reaction mixture) into standard hydrochloric acid was recorded to the nearest second, no zero time for the reactions being noted because of its irrelevance to graphic determination of the value of *k*. A constant volume of hydrochloric acid (always an excess) was used for the quenching of every sample in each series of runs and the excess was back-titrated with standard sodium hydroxide (*p*H meter). From six to eight samples were withdrawn in each run. Not less than three runs were made on each compound at each temperature (see Table IV).

Rate Calculations.—Calculations were based upon the equation: $1/(a - x) = kt + C$, in which a is the initial concentration of sodium methoxide in moles per liter and x is the moles per liter which have reacted in time t. The slope, calculated by the method of least squares, of the plot of $1/(a - x)$ *vs.* t for each run was taken as the value of k. Our assumption of second-order kinetics was substantiated by the straight line graphs which resulted.

In Table III we present a typical experimental record for the determination of the value of *k* in a particular run.

The values for the rate coefficients, obtained at 25, 35 and 45°, for the reactions of three 4-substituted-2-nitrochlorobenzenes with sodium methoxide in methanol solution are listed in Table IV.

From the equation[16a]

$$\log k = \log \frac{(ekT)}{h} - \frac{\Delta E}{2.303RT} + \frac{\Delta S^{\ddagger}}{2.303R}$$

values of ΔE were obtained by plotting values of log k against the reciprocal of absolute temperature. The three points in each plot fell virtually on a straight line. The slope, calculated by the method of least squares, was multiplied by $-2.303R$; the product was ΔE, the energy of activation. By substitution of the ΔE values so obtained, and of values of log k and of T for temperature 25° in the equation, and solving arithmetically, values of $\Delta S^{\ddagger}$, the entropy of activation, were found. These values of energy and entropy of activation are displayed in Table I.

Acknowledgments.—We take great pleasure in thanking the Research Corporation and the Office of Ordnance Research for generous financial support of this work, Professor C. K. Ingold for criticism of the manuscript, and Mrs. Bonnie Souther Robison and Messrs. Arnold Levitt and Robert Priest for assistance with some of the experiments.

PORTLAND, OREGON

[CONTRIBUTION FROM THE AGRICULTURAL CHEMISTRY DEPARTMENT, PURDUE UNIVERSITY]

Crystalline Xyloheptaose[1]

BY ROY L. WHISTLER AND CHEN-CHUAN TU

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Crystalline xyloheptaose, a linear β-1 → 4 linked oligosaccharide composed of xylopyranose units, has been isolated by charcoal chromatography from among the fragments produced by the partial hydrolysis of corn cob xylan. Xyloheptaose melts at 240–242° and has $[\alpha]^{25}D$ −74°. It is shown to be a member of the xylodextrin series.

Previously there has been described the isolation and characterization of a crystalline polymer-homologous series of oligosaccharides extending without interruption from xylobiose to xylohexaose.[2,3] The series is of particular interest since the members are composed entirely of pentose sugar units and because the members may be compared to the corresponding members of the cellulose series which are identical save for possessing a primary carbinol group attached to carbon atom C-5 of each ring unit.

Members of the xylodextrin series are obtained by chromatographic separation of partially hydrolyzed xylan. By extending these techniques it is now possible to separate, in pure crystalline form, xyloheptaose. This oligosaccharide can be obtained in a state of purity only by repeated purification.

The mixture of products obtained when xylan is partially hydrolyzed is roughly separated by charcoal chromatography[4] and the fraction richest in heptasaccharide is rechromatographed on charcoal. From this second chromatographic column may be selected an eluant fraction consisting of pure xyloheptaose which can be crystallized from 75% ethanol. X-Ray data indicate that the heptasaccharide is crystalline but has a crystal lattice almost identical to that of the hexasaccharide. The substance has a melting point of 240–242° which is only slightly higher than that of xylohexaose. A plot of melting point against degree of polymerization for the known xylodextrins is shown in Fig. 1. As is the case with other polymers the melting point

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[1] Journal Paper No. 648 of the Purdue Agricultural Experiment Station.

[2] R. L. Whistler and C.-C. Tu, THIS JOURNAL, **73**, 1389 (1951).

[3] R. L. Whistler and C.-C. Tu, *ibid.*, **74**, 3609 (1952).

[4] R. L. Whistler and D. F. Durso, *ibid.*, **72**, 677 (1950).